Amine Functionalized Cross-Linked Hybrid Full Color Phosphors Lacking Metal Activator Ions

L. D. Carlos[(1)], R. A. Sá Ferreira[(1)], V. De Zea Bermudez[(2)], and Sidney J.L. Ribeiro[(3)]

[(1)] *Departamento de Física, Universidade de Aveiro, 3810 Aveiro, Portugal*
[(2)] *Secção de Química, Universidade de Trás-os Montes e Alto Douro, Quinta de Prados, Apartado 202, 5001 Vila Real Codex, Portugal*
[(3)] *Instituto de Química - UNESP, C.P. 355, 14800-900, Araraquara-SP Brazil*
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White light tunable phosphors are obtained from a sol-gel derived siliceous network to which oxyethylene units are covalently grafted by means of urea or urethane cross-linkages. The bright photoluminescence is ascribed to an unusual convolution of distinct emissions originated in the NH groups of the urea or urethane bridges and in the siliceous nanodomains. The lifetimes of these emissions show a remarkable temperature dependence of approximately six orders of magnitude between $\approx$ 220 and 300 K associated with the hybrids glass transition temperature. This set of xerogels is one of the most surprising classes of full color emitters lacking metal activator ions.

I. INTRODUCTION

The synthesis of a wide range of novel materials by the sol-gel via has attracted considerable scientific interest in recent years [1–5]. In particular, the advantages (large variety and high purity of suitable precursors) of the rich chemistry of silicon-based networks have been employed to synthesize stable and efficient white light photoluminescent organic/inorganic hybrids lacking metal activator ions [6–13]. The outgrowth of full color displays, cheaper and less aggressive to the global environment, which could replace with substantial advantages the metal emissive centers currently used is one of the main challenging tasks for the next generation of flat panel display systems and lighting technologies. This aspect is well illustrated by the impressive impact of light emitting diodes based on conjugated polymers recently developed [14,15]. In spite of the potential technological relevance of the white light emission obtained from organically modified silicates, most of the research has been focused on the photoluminescence (PL) features of lanthanide-based hybrid matrices [3–5,7,16–20], seeking essentially to take advantage of the high chromaticity and long-excited lifetime characteristic of the metal ions, and of the improvement on the emission features and mechanical stability of the samples (compared to those of conventional silica gel hosts). As the hybrid matrices have been basically considered as an optically inert framework, only a limited amount of work has been directed to the study of their light emission features [6–13]. Since the publication of Canham's paper in 1990, demonstrating efficient tunable room temperature PL from porous silicon layers [21], the interest in light-emitting silicon-based materials has been significantly aroused [22]. The development of an optically efficient silicon-compatible material permitting optical and electronic devices to be completely integrated on a silicon wafer will certainly provoke a pronounced impact on displays, communications, computers and related technologies [23].

In this report, we discuss the origin of the PL features of stable and environmentally "friendly" innovative sol-gel derived hybrids containing OCH_2CH_2 repeat units grafted onto a siliceous backbone through urea, -NHC(=O)NH-, or urethane, -NHC(=O)O-, bridges. Since the synthesis of the former series of xerogels was first reported [24,25], several papers describing their PL features have recently appeared [7,8,11–13,17–20]. Yet, both the identification of the chemical species responsible for the white light emission and the characterization of the PL mechanism still remain controversial issues. We demonstrate here that the white light PL results from an unusual convolution of a longer-lived emission (10^{-1} s below 220 K) originated in the NH groups of the urea or urethane bridges with shorter-lived electron-hole recombinations (10^{-3} s below 220 K) that occur in the nanometer-sized siliceous clusters. Moreover, a remarkable temperature dependence of the two lifetimes is observed around the glass transition temperature, T_g, of the hybrids ($T_g \approx 220$ K). The longer-lived lifetime, for instance, steeply decreases to $\approx 10^{-6} - 10^{-7}$ s, when the temperature is increased from $200 - 220$ K to room temperature.

II. EXPERIMENTAL

A covalent cross-link between the 3-isocyanatepropyltriethoxysilane precursor, ICPTES (Fluka) and the oligopolyoxyethylene chains was formed by reacting the terminal amino groups of doubly functional amines (α,ω-diaminepoly(oxyethylene-co-oxypropylene), Fluka) or the OH groups of PEG (Aldrich), with the isocyanate group of the precursor in tetrahydrofuran (Merck) at room temperature and about 350 K, respectively. A urea- or urethane-based hybrid precursor was thus obtained [7,8,11-13,24,25]. Three diamines, commercially designated as Jeffamine ED-2001, Jeffamine ED-900, and Jeffamine ED-600, and PEG with different molecular weights are used. In the second stage of the synthesis process, the resulting hybrids were formed, adding a mixture of ethanol and water to the precursor solutions (molar proportion 1 ICPTES: $4\,CH_3CH_2OH$: $1.5\,H_2O$). The mixture was stirred in a sealed flash for 30 min and then cast into a Teflon mold and left in a fume cupboard for 24 h. After a few hours, gelation occurs and the mold was transferred to an oven at 310 K for a period of 7 days. The samples were then aged for 3 weeks at about 350 K to form white or yellowish amorphous and transparent monoliths, thermally stable up to 523 K that underwent bright PL. The hybrids have been classed, respectively, as di-ureasils, U(Y), and di-urethanesils, Ut(Y'), where Y=600, 900, 2000 and Y'=300, 2000 denote the average molecular weight of the starting diamine or of the PEG used.

The emission spectra were recorded ($14 - 300$ K) under continuous excitation with a 150 W xenon arc lamp coupled to a 0.25 m monochromator (Kratos GM-252) or an Ar ion laser (multi-line excitation 331.1 and 351.4 nm, 45 mW). A pulsed Xe arc lamp (5 mJ/pulse, 3 s bandwidth) and a SPEX 1934 C phosphorimeter are used in the time-resolved measurements. All spectra were corrected for the spectral response of the monochromator (1704 Spex) and the photomultiplier (Hamamatsu R928).

III. RESULTS AND DISCUSSION

The di-ureasil and di-urethanesil hybrids display a bright white light room-temperature PL (Fig. 1A), which is similar to the one detected for the corresponding diamines and the non-hydrolized organic/inorganic precursors (Fig. 1B). The emission of the diamines and the non-hydrolyzed di-ureasil precursors are identical demonstrating hereby that the formation of urea cross-linkages does not alter any of the PL features (Fig. 1B). After polycondensation and the building up of the inorganic network, a red shift of the PL maximum intensity is clearly observed (≈ 1061 cm^{-1} for U(2000), at an excitation of 365 nm, Fig. 1B). Yet, comparing the PL spectra for the two series of hybrids, the spectrum of Ut(2000) is blue-shifted with respect to the U(2000) one (≈ 1470 cm^{-1} at an excitation of 365 nm, Fig. 1B). When the excitation wavelength increases from 325 to 420 nm, the broad emission of the Jeffamines and urea- and urethane-based precursors is strongly shifted towards the red (not shown). This dependence is identical to the already reported behavior of the di-ureasils and di-urethanesils, permitting thereby the remarkably easy fine tuning of the hybrids color by varying only the excitation wavelength [11,13]. These results clearly indicate that the PL of the hybrids receives a major contribution from the NH groups. As no emission is detected from pure PEG, the PL must be related with the lone pair of electrons of the NH groups present in the diamines and in the non-hydrolized precursors, a claim which is in total disagreement with one reported very recently for similar hybrids [18].

The differences observed between the steady-state emission of the hybrids and that of the respective precursors are well established by time resolved spectroscopy measurements. For delay-times smaller than 5 ms, while the U(2000) and Ut(2000) spectra unambiguously display two bands in the blue and purplish-blue spectral regions [11,13], only a single large broad band is seen in the spectrum of Jeffamine ED-2001, Fig. 2. For the diamines and the non-hydrolyzed precursors there is no evidence of the presence of the band that clearly appears centered at about ≈ 425 nm in the time-resolved spectra of all the five hybrids. Besides having different intrinsic time scales, the two bands in the di-ureasil and di-urethanesil spectra also exhibit a distinct behavior when the excitation wavelength is increased from 325 to 420 nm (Fig. 3). The blue band is evident over the whole excitation wavelength range, the location of its intensity maximum strongly depending on the excitation wavelength. The purplish-blue band, which displays no energetic position dependence with the excitation wavelength, could be detected only between 350 and 375 nm (Fig. 3).

For all the five hybrids, the 14 K blue and purplish-blue band lifetimes are ≈ 160.0 and ≈ 3.5 ms, respectively (errors within $3-5\%$), in the whole range of excitation wavelengths used. The observed lifetime for the Jeffamines, at the same temperature and excitation wavelengths, is ≈ 120.0 ms ($\pm 3 - 5\%$). By increasing the temperature up to 220 K, the lifetime of the purplish-blue band displays a typical Arrhenius behavior with temperature (not shown). On the contrary, the long-lived lifetime of the hybrids and of the diamines oscillates around the low temperature value, therefore displaying no significant temperature dependence within this range (not shown).This is another apposite argument supporting the above assumption that the blue component of the xerogels emission is fundamentally related to the NH groups of the cross-links. A noteworthy aspect in these measurements is the abrupt decrease of the lifetimes above $200-220$ K, nicely illustrated by the set of real time frames of Fig. 4. For temperatures higher than ≈ 220 K, the lifetimes lie in a time scale smaller than 10^{-5} s, being around 10^{-8} s at room temperature [18].

The PL characterization of the Jeffamines, urea- and urethane-based non-hydrolized precursors, and the di-ureasil and di-urethanesil hybrids furnish persuasive arguments that the full color emission must involve the NH groups. Furthermore, we have presented strong evidence that grafting the NH$_2$ or OH groups to the isocyanate group - with the subsequent formation of urea or urethane cross-linkages, respectively - does not alter significantly the emission features. Nevertheless, a new band with completely distinct features is detected, after gelation. Based on small-angle X-ray scattering (SAXS) results the morphologies of the di-ureasil and di-urethanesil hybrids were depicted as a diphasic structure constituted of dispersed and spatially correlated siliceous nanoclusters embedded in the polymer matrix and located at the ends of the organic chains [11,26]. As a result, the purplish-blue component must be unquestionably related to the silicon-rich nanodomains. This can be further confirmed by altering the conditions at which the hydrolysis and condensation reactions occur, thus modifying the local structures of those siliceous nanoregions. For the di-ureasils and di-urethanesils reported here, ^{29}Si magic-angle spinning nuclear magnetic ressonance spectroscopy (MAS NMR) has established the presence of essentially two structures, (SiO)3Si(CH2)- and (SiO)2Si(OH)(CH2)-, surrounding the Si atoms [13]. A new U(600) di-ureasil sample was synthesized using a different ICPTES:CH$_3$CH$_2$OH:H$_2$O ratio, which alters both the condensation degree and the relative proportions between the two local Si surroundings, as ^{29}Si MAS NMR results indicate (not shown). The 14 K time-resolved spectra for that hybrid displays a long-lived blue band similar to the one observed in all the other samples (not shown). However, a new short-lived band, centered around 450 nm, is detected on the purplish-blue region, supporting the suggested influence of the siliceous nanoclusters on the full color emission detected.

Recently, the origin of the strong PL detected in an organic/inorganic hybrid very similar to the U(900) di-ureasil - the only differences in the two synthesis procedures being the use of NH$_4$F as a catalyst and a distinct Si:H$_2$O molar

proportion - was explained in terms of the introduction of carbon impurities in the -Si-O-Si- network during hydrolysis-condensation reactions [18]. A similar carbon defect has been previously assumed to be responsible for the PL of hybrid matrices made from the reaction of tetramethoxysilane and tetraethoxysilane with a variety of organic carboxylic acids [6]. The creation of a carbon substitutional silicon defect needs, however, a heating process at temperatures above 520 K, at least [6]. Moreover, water-soluble hybrids generated from the reaction of (3-aminopropyl)triethoxysilane with a variety of organic carboxylic acids do not require any heating process above 330 K to be luminescent. Accordingly, the luminescent species must be different than carbon defects and the white light emission of APTES-derived hybrids was related to the presence of amide functionalities [6]. All the PL results of the di-ureasils and di-urethanesils are in agreement with that hypothesis, stressing, therefore, the significant role of the lone-pair of the NH groups in their white light emission.

A final comment regarding the remarkable and drastic decrease of $5-6$ orders of magnitude in the lifetimes, at temperatures ≈ 220 K. This critical temperature region concerning the lifetime determination is exactly the one associated to the T_g of the OCH_2CH_2 repeat units. Below T_g, the emitter centers related to the NH groups are quenched in a particular configuration, decreasing, therefore, the non-radiative deexcitation paths induced by the segmental mobility of the polymer chains. When the temperature is raised above ≈ 220 K there is an obvious enlargement in the segmental mobility of the polymer chains (and consequently in the NH_2 chain end-groups) with the subsequent increase in the possible non-radiative deexcitation channels.

IV. CONCLUSIONS

The interest in organic-inorganic hybrids is basically associated with the extraordinary implications for the tailoring of novel multi-functional advanced materials induced by the mixture at the nanosize level of organic and inorganic components in a single material. The synergy of that combination and the particular role of the inner interfaces open up exciting new areas in materials science and related technologies. The bright full color room temperature PL reported here being an unforeseen example that nicely illustrates the effects on the optical features of hybrid materials that could be obtained by the grafting of organic and inorganic components in a single material. The surprising and unusual convolution of distinct emissions originated in the NH groups and in the nanometer-sized siliceous domains, the ability to tune those emissions to colors across the chromaticity diagram, and the remarkable temperature dependence $(220-300$ K) of their lifetimes are innovative features emphasizing the potential of these hybrids on display silicon-compatible technologies requiring red, green and blue devices.

ACKNOWLEDGMENTS

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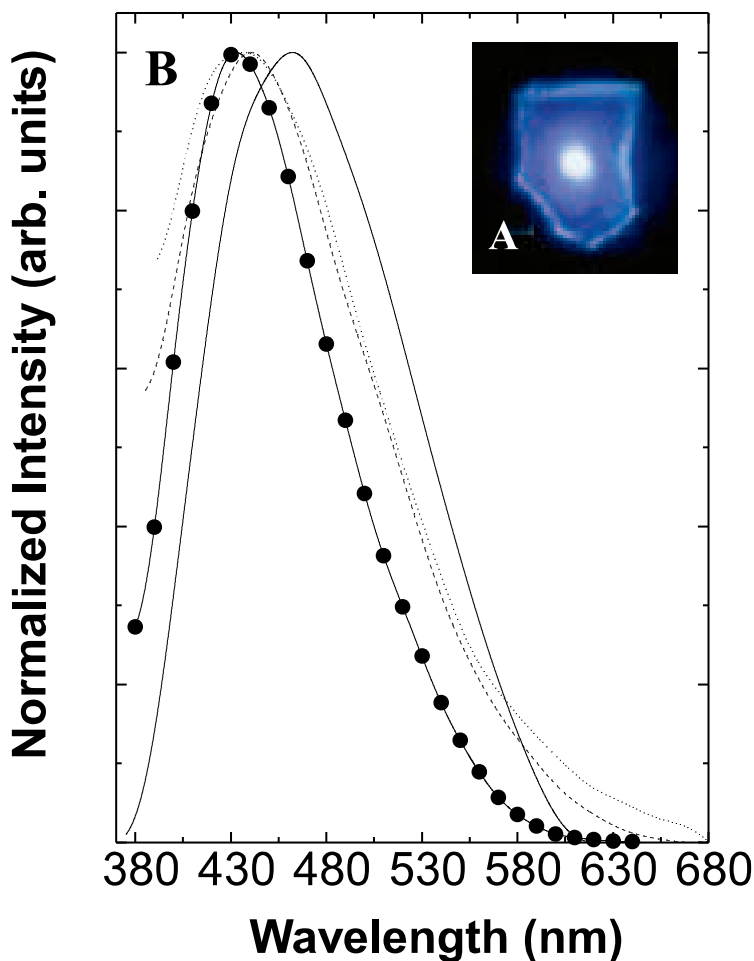
FIG. 1. A: A photograph showing the white light emission of U(2000) at 298 K under UV excitation (Ar ion laser). The diameter of the emitting area is ≈ 3 mm^2. B: PL spectra (365 nm excitation at 298 K) of representative amine-based functionalities, precursors and di-ureasil and di-urethanesil hybrids: Jeffamine ED-2001 (dashed curve), non-hydrolyzed Ut(2000) precursor (dotted curve), U(2000) (solid curve), and Ut(2000) (solid curve with circles).
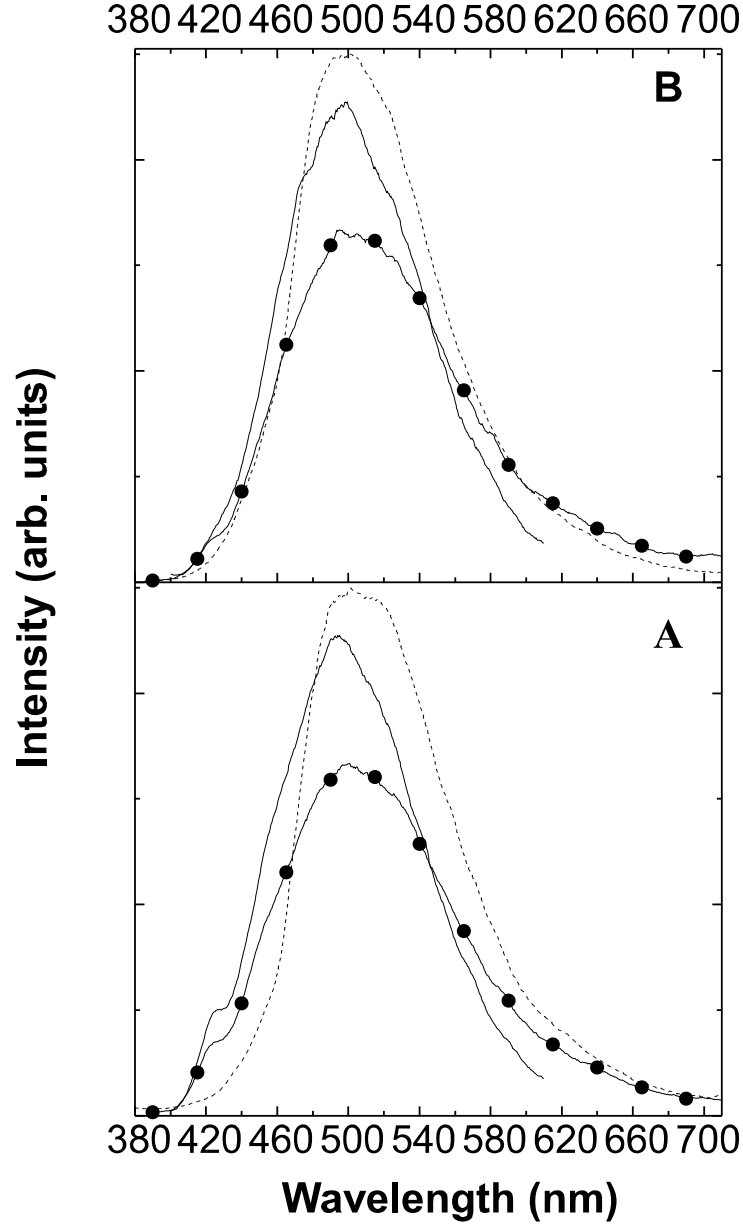

FIG. 2. Time-resolved spectra (365 nm excitation at 14 K) of Jeffamine ED-2001 (dashed curve), U(2000) (solid curve), and Ut(2000) (solid curve with circles) measured at a fixed acquisition window, 10 ms, and different delay-times, A: 0.08 ms, B: 5 ms.
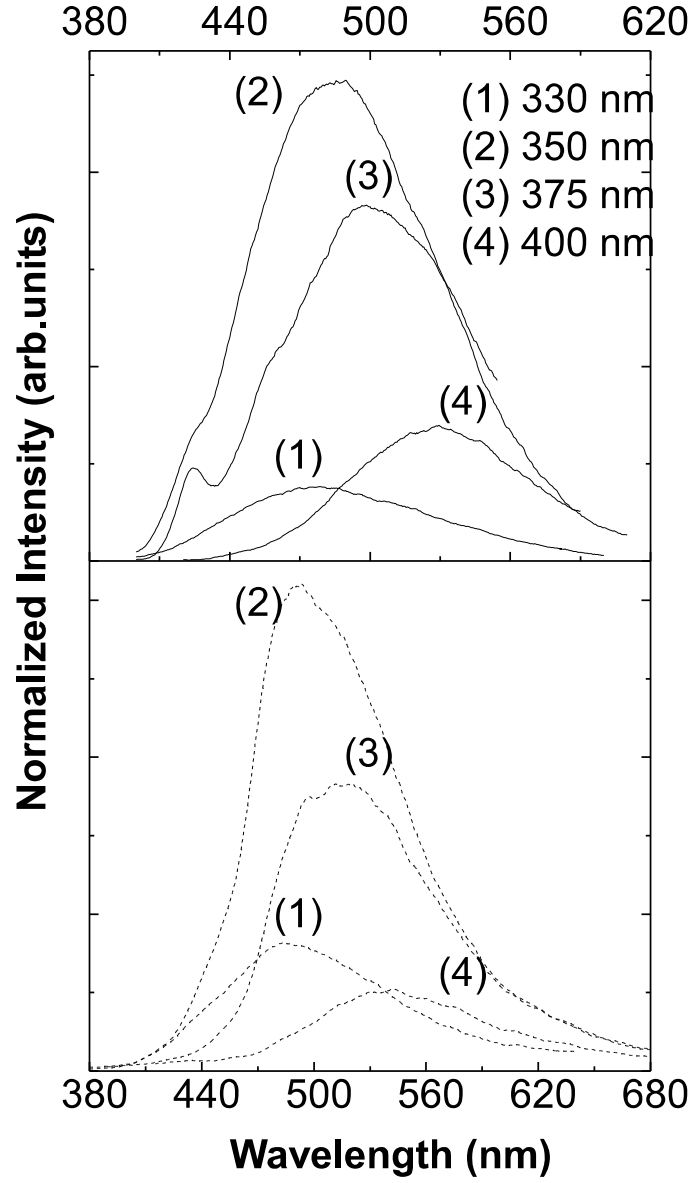
FIG. 3. Time-resolved spectra (0.08 ms delay-time, 10 ms acquisition window at 14 K) for U(2000) (solid curves) and Jeffamine ED-2001 (dashed curves) obtained for different excitation wavelengths.
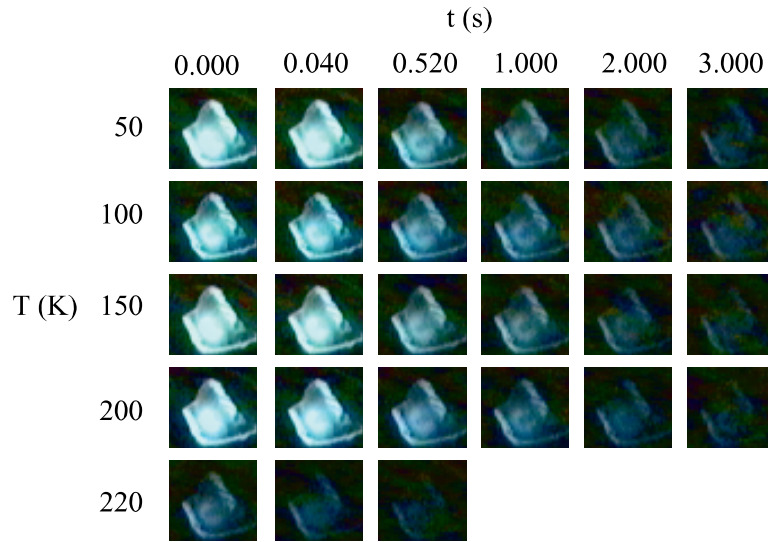
FIG. 4. A set of frames showing the real time dependence (14 − 220 K) of the U(2000) white light emission during 3 s after the Ar laser beam was turned off. Note that the emission color is slightly distorted by the video camera. The real color is more "whitish-blue", Fig. 1A.